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Method for Measuring Carbon Fiber Emissions from Stationary Sources

Battelle Columbus Labs., OH

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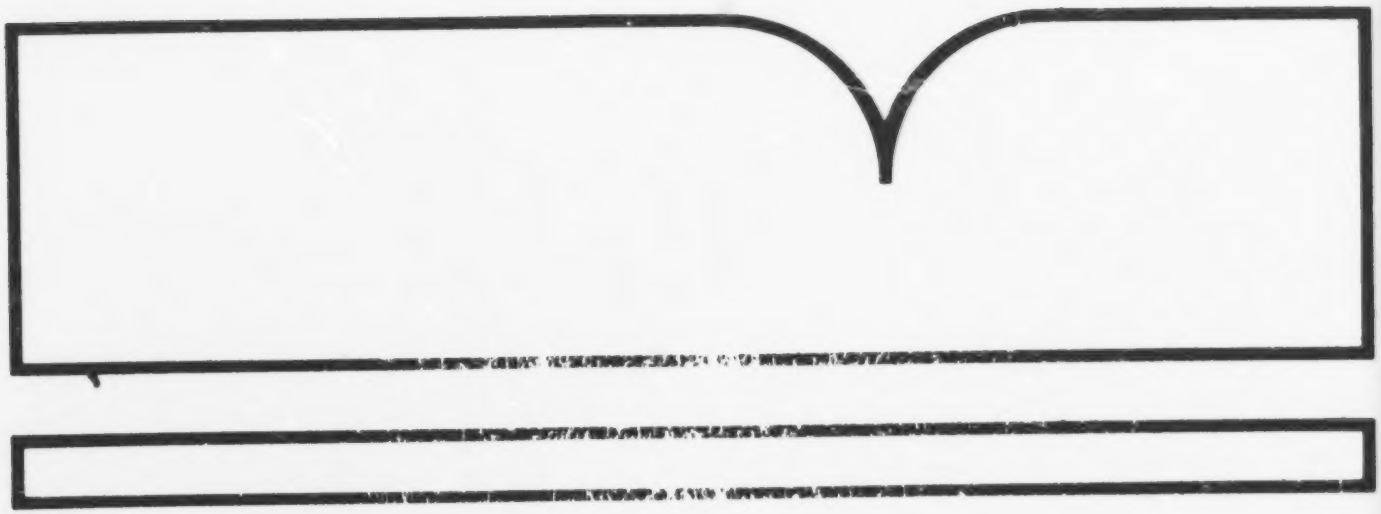

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METHOD FOR MEASURING CARBON FIBER EMISSIONS FROM STATIONARY SOURCES

by

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16. ABSTRACT

Carbon fibers are highly conductive, lightweight and of small dimensions. When released as emissions from production, manufacturing, processing and disposal sources they may become airborne and disperse over wide areas. If they settle onto electronic or electrical components they can cause malfunctions and damage due to their high electrical conductivity. This research program was initiated to develop techniques to identify and measure carbon fiber concentrations emitted from manufacturing, processing, fabricating and incinerating sources. Its overall objective was to develop a measurement method useful to support possible emission regulatory actions.

A method based on light microscopy was selected for test and development since fiber count and fiber size range were required, as well as total fiber mass concentration. Experimental work, carried out on laboratory and field site samples, showed that carbon fibers could be readily recognized and counted without extensive separation from other particulate "debris" collected during source sampling. Fibers were reduced in diameter during oxidative and thermal processes such as incineration but the size reductions were not such to be beyond the resolution power of light microscopy.

The method was tested on samples collected from various stationary emission sources and from a pilot-scale in-house incineration facility. The results of these emission measurements are reported.

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ABSTRACT

This research program was initiated to develop techniques to identify and measure carbon fiber concentrations emitted from manufacturing, processing, fabricating and incinerating sources. Its overall objective was to establish a method useful to support possible emission source regulatory actions.

A method based on light microscopy was selected for test and development since fiber count and fiber size range were required, as well as total fiber mass concentration.

Experimental work, carried out on laboratory and field site samples, showed that carbon fibers would be readily recognized and counted without extensive separation from other particulate "debris" collected during source sampling. Fibers became thinned during oxidative and thermal processes such as incineration but the size reductions were not such to be beyond the resolution power of light microscopy.

The method was tested on samples collected from various stationary sources and on samples collected from a large in-house incineration facility and the results of these emission measurements are reported.

This report was submitted in fulfillment of Contract No. 68-02-3229 by Battelle's Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 16, 1979, to January 15, 1981, and work was complete as of February 28, 1981.

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SECTION 1

INTRODUCTION

A potential environmental problem has been foreseen arising out of the rapidly developing usage of carbon, or graphite* fibers incorporated into resin matrix composites.[1,2,3] These graphitized carbon fibers are fine diameter (5 to 10 μm typically), very lightweight (1.5 to 2 g/cc), chemically inert, and very excellent electrical conductors (resistivity between 1×10^3 and 25×10^3 ohms/cm of fiber length). Because of these properties the fiber filaments, when separated from their composite forms, can be readily airborne and transported long distances by normal atmospheric motion. The principal environmental concern arises out of the potential of these released fibers to come in contact with electrical and electronic components and cause short circuits, arcing, and otherwise damage or destroy equipment performances. Manufacturers, processors, and fabricators of carbon fibers and composites are generally aware of these potential hazards and take control measures to minimize fiber emissions. Despite these measures fiber release does occur during fiber forming, fiber chopping, rewind operations, composite formation, and subsequent shaping by grinding, sawing, drilling and cutting. Additional fiber contamination hazards can occur during waste disposal of consumer goods and industrial scrap by incineration processes which thermally decompose the matrix material and release fibers into the atmosphere via stack emissions.

While current production and usage of carbon fiber composites (estimated as less than 500 tons in 1980) may present only a limited hazard now, large increases in demand are foreseen for these lightweight, high-strength materials, especially in the aircraft industries and projected future automotive uses in order to achieve fuel savings via weight reductions. For this reason the Federal Government has instituted various programs to study all aspects of potential problems associated with carbon fiber production, usage, and disposal. As a part of these plans, the U.S. Environmental Protection Agency has initiated several investigative, developmental, and research studies related to carbon fibers as a potential pollutant problem, including the program described here. To date no direct health effect problems have been identified with carbon fibers. The risk potential for carbon fibers

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* Carbon fibers are used as a general term in this report to include both carbon and graphite fibers resulting from pyrolysis of fibrous materials which have been heat treated to temperatures higher than the decomposition temperature of the precursor polymer--typically 1000 to 1200 C for carbon fibers and above 2000 C for graphite fibers.

released to the atmosphere stems principally from hazards due to the potential for carbon fibers interference with electrical and electronic systems and this should be relatable to the size range, number, and mass of fibers emitted. Fibers with a length-to-diameter ratio of 5 to 1 and greater were of primary concern in this program, although the research investigation showed that particles of lower length-to-diameter ratios could be identified and counted readily.

Little data are available in the open literature as to the emission rates and resulting atmospheric concentrations of carbon fibers but some counts of other man-made and asbestos fibers are available for comparisons. According to a carbon study group report[1], in 1974 the U.S. Public Health Service reported on airborne particulates from ten fibrous glass production facilities. These are given in Table 1, together with OSHA occupational exposure limits on asbestos and NIOSH recommendations on total fiber exposure limits. Some measurements, made to determine the concentrations (number and mass) of carbon fibers needed to cause malfunctions in electrical equipment, indicated that medium (18 to 500) and high (>500) voltage electrical interferences seem to begin in an exposure range of 10^5 to 10^7 fibers/m^3.[4] At the other extreme, single fibers have been found to cause shorts or initiate arcing at low (<30) voltage.

TABLE 1. OTHER SMALL-DIAMETER FIBER EMISSIONS AND EXPOSURE LIMITS

Fiber types	Observed Airborne Fiber Counters
Large-diameter glass fibers Mean diameter 1.1 to 4.3 μm	60,000 to 130,000 fibers/m^3 Mean dust conc. 0.34 to 2.74 mg/m^3
Small diameter glass fibers Mean diameter 0.1 to 2 μm	1,000,000 to 21,900,000 fibers/m^3 Gravimetric concentration <1 mg/m^3
Asbestos fibers, 8-hour average (OSHA permissible exposure)	2,000,000 fibers/m^3
Total fibers >3.5 μm diameter and 10 μm length and less (NIOSH recommendation for 10-hour workshift)	3,000,000 fibers/m^3

This study has focused on the development of a method for the positive identification and determination of carbon fiber concentrations emitted from various types of stationary sources. Sampling of carbon fiber emissions was done using commonly employed sampling techniques; namely, an open-face filter collection mode[5] for emissions from winding, weaving, machining and pre-pregging sources and a EPA Method 17 and Source Assessment Sampling System trains for incinerator stack source sampling. The experimental studies included:

1. Trials of various modes of separation of carbon fibers from other particulate contained in source emissions.

2. Validation of light microscopy as a means for routine identification of carbon fiber emissions.

3. Measurements of carbon fiber mass, number and size distribution in emission collections from manufacturing, processing and pilot plant incineration source.

4. Preparation of a detailed analytical procedure based on light microscopy.

SECTION 2

CONCLUSIONS

Based on experimental work with laboratory-prepared and field site emission collections, including those from a pilot-scale in-house incineration facility, the following conclusions have been reached:

1. Carbon fiber emissions are of sufficiently large dimensions to be resolved and positively identified by light microscopy.

2. A light microscopy analytical method can provide a measure of the mass, fiber count and fiber sizes present in emission collections.

3. Extraneous particulate matter, including other fiber types collected with the carbon fiber emissions, does not interfere with the carbon fiber identification measurements so rigorous separation procedures are not required in the method.

4. The use of a membrane filter as a collection medium is desirable since this filter type can be removed readily from the particulate collections by use of a nitric acid digestion treatment prior to the microscopic analysis.

5. The use of cyclones, such as in a SASS train, is useful in sampling at incineration sites where a membrane is not thermally stable, and a quartz or glass filter must be used. In the limited incineration sample tests done, over 99 percent of the carbon fiber emission mass was collected in the cyclones from which the fibers could be easily brushed out for analysis.

6. The developed methodology is compatible with the personnel skills and equipment available at most Federal and local regulatory and industrial testing laboratories.

7. Data obtained in samples collected at carbon fiber manufacturing and processing operations showed carbon fiber emissions to range from 24 to 1200 fibers/m^3 with average lengths from 48 to 750 μm.

SECTION 3

RECOMMENDATIONS

As with any technique based on microscopy, the skill and experience of the operator is paramount in obtaining reliable data. It is recommended that the precision and accuracy of the analytical method be established for each operator. Intercomparisons of such data should be obtained among the laboratories as well.

Repetitive tests of the sampling methods should be performed to establish the precision and accuracy of these.

Further experimentation should be carried out on the use of cyclones preceding a back-up filter as a mode of sampling carbon fiber emissions from manufacturing and processing sources as well as from incineration sources. Although it has been found that the presence of particulate matter additional to carbon fibers in the sample collections does not present an undue problem in the analysis, the time required to identify and count fibers might be lessened and the accuracy of the methodology improved if most carbon fibers were found to be contained in the cyclone components of a sampling train with a minimal number of fibers on the filter.

SECTION 4

EXPERIMENTAL PROGRAM

GENERAL CONSIDERATIONS

Based on our experience in the development and application of analytical methodology for other fiber materials, notably asbestos, it appeared obvious that a microscopic fiber counting and measurement method would produce reliable results. Unlike asbestos, carbon fibers are sufficiently large (5 to 10 μm diameters) to be detected by light microscopy which requires lesser skills and is far more rapid than electron microscopy, necessary for identification of the much finer diameter asbestos fibers. (Fiber diameters of 0.5 μm can be detected readily by light microscopy.) A light microscopy method would be especially effective when preceded by a technique to separate carbon fibers from other inorganic and organic particulate matter collected by the source sampling system. The prospect of separating carbon fibers from other emission particulate matter, or at least enriching the carbon fiber content of a collection relative to other inorganic and organic species appeared good. Carbon fibers are resistant to acid attack. This suggests that acid soluble particulate matter could be digested and removed from the chemically inert carbon fibers. Thermal ashing might be used to rid sample collections of readily volatile materials such as organic matter and possibly other carbonaceous matter. Carbon fibers, being naturally hydrophobic, can be separated from inorganic particulate matter by a two-phase liquid separation procedure. The higher density of carbon fibers represents another mode of separation from carbon black, soot, and other carbonaceous matter.

Criteria for Method

To fulfill the requirements of the contract program, the carbon fiber emission method should:

- Be specific for carbon fibers
- Provide for measurements of both mass and numbers of fibers per unit volume of sample or per unit mass of sampled particulate
- Be acceptable for testing for application as a reference method to support a potential emission standard.

The method selected for trial as best suited to meet these requirements was based on use of light microscopy to identify and measure carbon fiber lengths and widths. Using these data, total carbon fiber mass and number of

fibers per unit volume or mass rate of emissions can be calculated. Also plots of fiber length, width, and length/width ratio can be generated to show size distribution as a function of cumulative number percent and cumulative volume (or mass) percent.

To validate a light microscopy method as an analytical method specific for carbon fibers, several criteria must be met including:

(a) The fibers must be unequivocably distinguishable from other fibers and particulate emission species.

(b) The fibers must be of dimensions within the resolution of light microscopy (0.5 μm and >).

(c) The integrity of the carbon fibers must be preserved during the sample preparation steps prior to the identification and counting procedures.

(d) The carbon fibers must be collected or redeposited uniformly on a suitable substrate in order to provide quantitative determination by viewing and measuring representative portions of the collections in the light microscope field.

ANALYTICAL METHOD DEVELOPMENT

Removal of Extraneous Material

Thermal Treatments--

Low temperature oxygen plasma and microwave heating were tried on representative PAN and pitch carbonized and graphitized fibers to thermally remove organic and readily volatile inorganic particulate matter. When sufficient power was applied, the fibers were totally destroyed. Nearly immediately under microwave radiation, on application of the RF power, the fibers apparently were heated so rapidly that they absorbed energy and exploded, giving off flashes of light as they vaporized and disintegrated. It appears that the frequency coupling and resultant light flashes which occur upon exposure of carbon fibers to microwave radiation might provide a basis for the development of a rapid analytical screening or monitoring method to show the presence of carbon fibers among other particulate debris. Possibly microwave energy might provide for use as a dynamic or on-the-fly method by drawing an air stream through a microwave energized field and measuring the light flashes. However, this possible approach to identification of carbon fibers in source emissions was not pursued because of the extensive experimental efforts required to ascertain the feasibility of the technique.

More conventional thermal treatment was investigated as a means of separation. Experiments were conducted by heating at 600 C in air for varying time periods in order to remove the particulate matter.

Four types of carbon fibers were used in the study; one was a graphitized fiber and the others were carbonized fibers. Only a Hercules PAN TOW

carbonized fiber was unaffected by the treatment. Even the graphitized fiber was thinned to approximately one half its original diameter in one hour at 600 C. The Kreha carbonized pitch fiber was found to be thinned the most but none were thinned by the treatments given to the degree that electron microscopic analysis would be mandatory. Results of the thinning studies expressed as mean widths are presented in Table 2.

The consequence of carbon fiber thinning and disintegration during heating with respect to the development of analytical procedures remained of concern. Fiber diameters ranging from 0.5 μm upward can be detected with the light microscope. However, varying degrees of oxidation of carbon fibers can occur during incineration, and as a result, various fiber sizes will be present and it is possible that very thin fibers could escape detection. Further investigations were made of the effects of heating at 600 C in air on Kreha pitch TOW carbonized fiber which was found very susceptible to oxidation. Specimens were prepared for electron microscopy of the oxidized fiber heated at 600 C for 15 minutes. At this point, at least half of the fibers had been completely oxidized. Fibers of a size which could be detected only by electron microscopy, if such fibers will remain intact, should have been present in this specimen. None were seen. Apparently they had entirely disintegrated. Only fiber sizes that could be detected with the light microscope were observed. However, the fibers after heating in air were no longer straight. Figure 1 shows one unaltered straight fiber among other fibers which have been curled by heating in air.

The progression of oxidation of fibers emitted from PAN composites during simulated incineration was studied further by scanning electron microscopy. Fibers subjected to varying degrees of oxidation were produced by nonuniform heating in a Fisher burner flame. Scanning electron micrographs were taken which revealed the development of dimples on the fiber surface.

The mechanism by which the dimples are produced appears to be related to the formation of subsurface gas pockets in the carbon fiber from which the gas erupts to create craters in the fiber surface. The craters are selectively oxidized, possibly because they present more surface area, to form the dimple structure that is characteristic of incinerated carbon fibers.

As oxidation proceeds, relatively short lengths of thinned carbon fibers result from preferential oxidation at dimple sites until the fiber is completely severed. At the same time, slower overall oxidation occurs which results in relatively uniform thinning down to fiber diameters of ≈ 1.0 μm.

The progression of oxidation of PAN carbon fibers is shown by electron micrographs in Figures 2 through 7. No fibers thinner than 1.0 μm occur. In view of the susceptibility of thermal treatments to alter the integrity of the carbon fibers, this technique was dismissed as a technique to separate carbon fibers from other emission particulate species.

Two-Phase Liquid Separation--

A two-phase liquid separation (TPLS) was tried as a means of separation of carbon fibers from other particulate matter. This technique had been applied

TABLE 2. EFFECTS OF HEATING FIBERS AT 600 C IN AIR ON FIBER DIAMETERS

Sample No.*	Mean Width, μm		Variance, μm		Time
	Pre-heat	Post heat	Pre-heat	Post heat	
1	$6.7 \pm 0.7^{(a)}$		0.16		--
		$3.4 \pm 1.8^{(b)}$		1.0	1 hr
3	$6.4 \pm 0.3_{(a)}$		0.03		--
		$6.7 \pm 0.8^{(b)}$		0.2	1 hr
4	$16.4 \pm 1.8^{(a)}$		0.90	--	--
		$16.9 \pm 2.5^{(b)}$		1.9	5 min
		$17.1 + 2.2^{(b)}$		1.4	10 min
		$9.1 \pm 2.5^{(b)}$		1.9	15 min
		$5.1 \pm 4.5^{(b)}$		6.2	20 min
		$8.1 \pm 4.0^{(c)}$		4.9	1 hr
5	$13.2 \pm 1.9^{(a)}$		1.1		--
		$11.5 \pm 2.6^{(b)}$		2.0	1 hr

(a) Based on 75 fibers.
(b) Based on 100 fibers.
(c) Based on 25 fibers.
*No. 1 - Union Carbide Rayon Base TSO Graphite.
No. 3 - Hercules PAN TOW Carbonized.
No. 4 - Kreha Pitch TOW Carbonized.
No. 5 - Union Carbide Pitch Fiber Carbonized.

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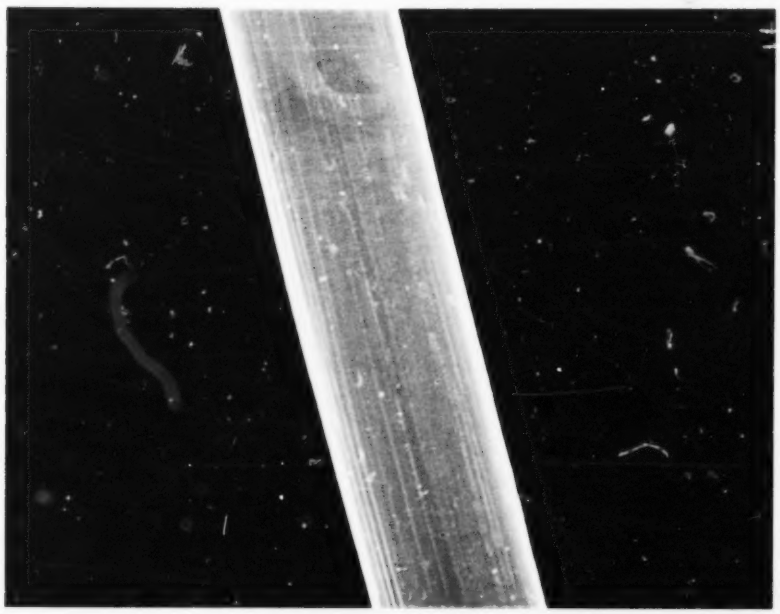
100 X

Figure 1. Kreha pitch tow carbonized fibers after heating at 600 C for 15 minutes.



3000X

Figure 2. An unoxidized carbon fiber.

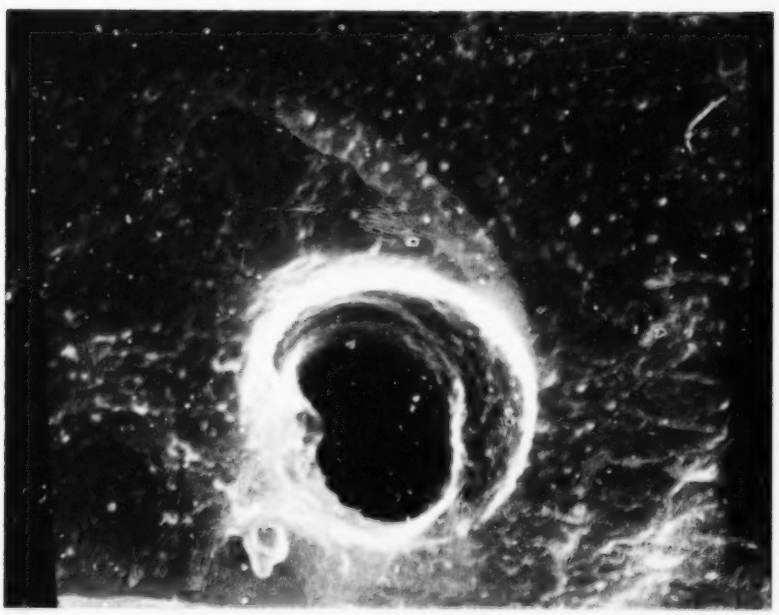


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Figure 3. A crater formed in the surface of a fiber probably by the eruption of gas from a subsurface pocket.

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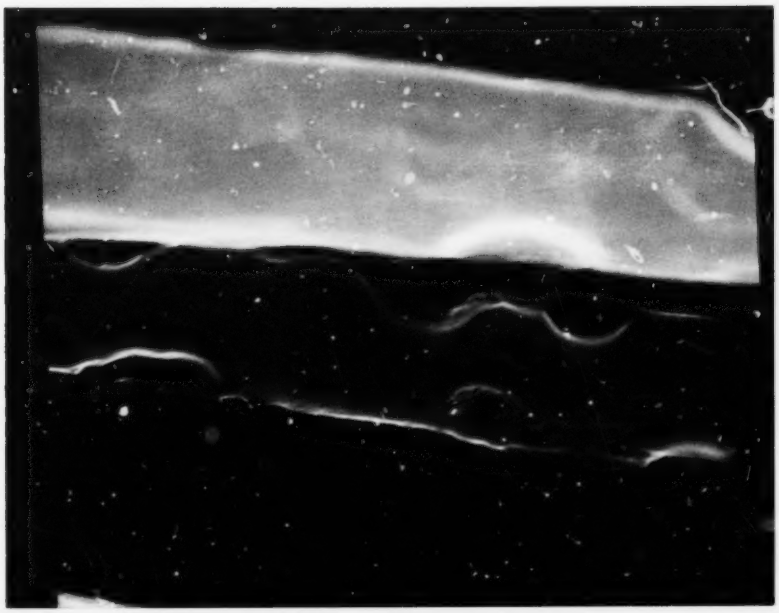

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Figure 4. Typical dimples created by selective oxidation.

3000X

Figure 5. Selective oxidation has almost severed fiber.

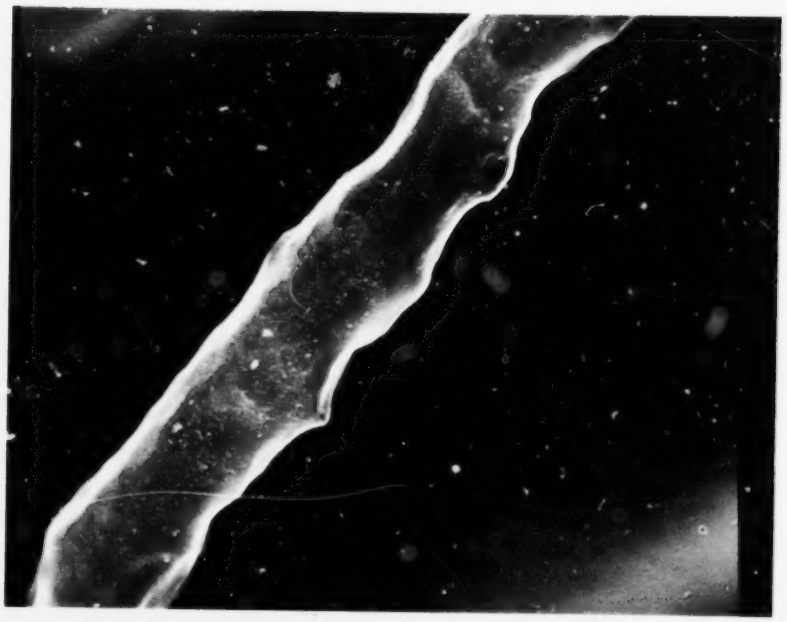

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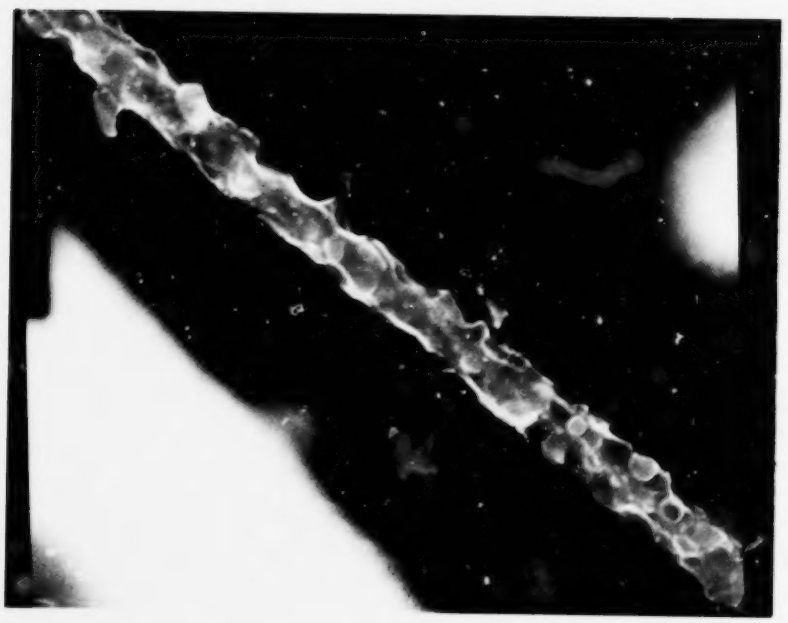
Figure 6. Irregular fiber shape due to selective oxidation.



10,000X

Figure 7. A severely oxidized fiber thinned to approximately 1.0 μm in diameter.

with some success in the development of an analytical method for determining asbestos in water.[6] Essentially, TPLS selectively extracts the carbon fibers from a water suspension of particulate matter (incineration ash was used) into a water-immiscible organic liquid. The more hydrophobic carbon fibers can be extracted from the water suspension into the organic phase by shaping in a separatory funnel. Initial experimentation showed the carbon fibers collecting at the water-organic liquid (isooctane) interface. Subsequent experimentation using a surfactant (Triton X) resulted in a majority of the fibers remaining in the organic phase. Using extreme care, a fairly high degree of separation was achieved, but the extraction procedure required considerable skill and time and reproducible results were not obtained. In view of the relative ease with which carbon fibers could be identified without extensive separation efforts, TPLS efforts were not pursued in more depth.

Wet Ashing--

Acid digestion appeared to offer a useful mode of separating carbon fibers from other particulate matter contained in sample collections. The ASTM D 3171, Standard Test Method for Fiber Content of Reinforced Resin Composites, utilizes hot nitric acid or a sulfuric acid - hydrogen peroxide mixture as digestion media to rid the resin from composites prior to weighing the unattacked carbon fibers. Hot nitric acid should digest most of the organic and soluble metal salts contained in particulate matter samples, facilitating the identification and counting the chemically inert carbon fibers. Several experiments were performed to check that the nitric acid treatment would not affect the integrity of the carbon fibers.

Four types of carbon fibers (listed below) were subjected to treatment in boiling concentrated nitric acid. The fiber types are:

(1) Union Carbide Rayon Base TSO Graphite.

(2) Hercules PAN TOW Carbonized.

(3) Kreha Pitch TOW Carbonized.

(4) Union Carbide Pitch Fiber Carbonized.

In each experiment, a piece of filter paper was treated along with the carbon fiber sample to determine if the paper would be destroyed by the treatment. Measurements of fiber diameters were made after "wet" ashing. The conditions in hot nitric acid destroyed the paper, but did not alter the fiber diameters of any of the carbon fiber samples. Additional experiments were conducted in which carbon fibers were intermixed with particulate matter and the mixture treated with hot nitric acid. Subsequent light microscopic examinations showed a considerable amount of the particulate matter was digested but the carbon fibers appeared unaffected by the acid treatment.

Some concern was felt that this nitric acid treatment might attack oxidized carbon fibers, especially those that had been recovered from an incineration process stack emission, and thus change the fiber sample dimensions. As a check on the possible attack by use of nitric acid, carbon fibers which had been contained in a composite were treated in a muffle furnace at 900 C

for 20 minutes. After this thermal treatment, the fibers were found to have lost about half of their original mass and were noticeably diminished in diameters - see Figures 8 and 9. The carbon fiber samples, as represented by Figures 8 and 9, were examined microscopically before and after the nitric acid treatment and no structural changes were observed.

Carbon fibers collected by a cyclone sampler from a refuse-carbon composite incineration experiment, described later in this report, also were treated with hot nitric acid and examined microscopically with no change in fibers observed. See Figure 10 and 11 for comparison.

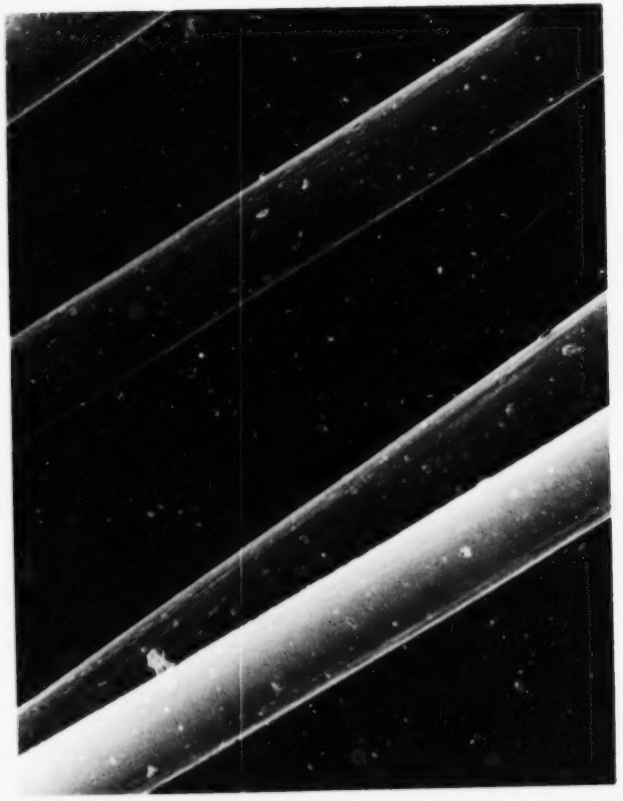
The use of nitric acid in the analytical procedure has a more important advantage in the analytical procedure, namely, in the treatment of the filter media used for sample collection. A mixed cellulose ester membrane filter (Millipore) was used for sample collection, except at incineration sources where a more thermally stable filter is required. To yield quantitative data, the particulate matter collected by sampling must be distributed uniformly throughout the fields of view examined by the light microscope. This was best achieved by placing the sample filter into an aqueous solution, adding hot concentrated nitric acid to digest the membrane filter substrate, diluting the solution to a weakly acidic state, agitating the slightly acidic liquid to obtain a uniform suspension of the particulate matter, and then vacuum filtering the suspension liquid through another 0.45 μm pore size Millipore filter. This resulted in a uniform distribution of the sample suitable for counting and measuring in the light microscope. The diluted, cold nitric acid altered the second Millipore filter slightly but it still functioned as a filter. The principal advantage of use of nitric acid is to get rid of the collecting filter prior to transferring the sample from the collection filter to the aqueous media and then to a uniform dispersement onto a second filter for analysis, but the removal of acid soluble particulate matter as well simplifies the microscopy work.

APPLICATION TO SAMPLES

Field Collections: Manufacturing and Processing Sites

As an aid in development as well as a practical test of the applicability of the subject techniques, field collections of carbon fiber emissions from several processes were made and subjected to analysis. Typical worker exposure and outside emissions from winding, prepregging, weaving and machining operations were sampled. Analysis of samples showed carbon fiber concentrations ranging from 200 ng/m^3 to 6800 ng/m^3 with the developed techniques proving applicable for all samples collected. The carbon fiber was PAN fiber in each of the situations sampled.

The sampling procedure used in each circumstance was the same. This procedure involved drawing the fiber-laden air through high-efficiency membrane filters with a vacuum pump. A 5.0 μm pore size cellulose acetate membrane (Millipore) filter was the substrate used for fiber collection. To facilitate analysis, 47-mm diameter filters were employed using an open-faced filter holder. The sampling flow rate was set and fixed at a suitable level



2000 X

Figure 8. Carbon fibers from pan composite.

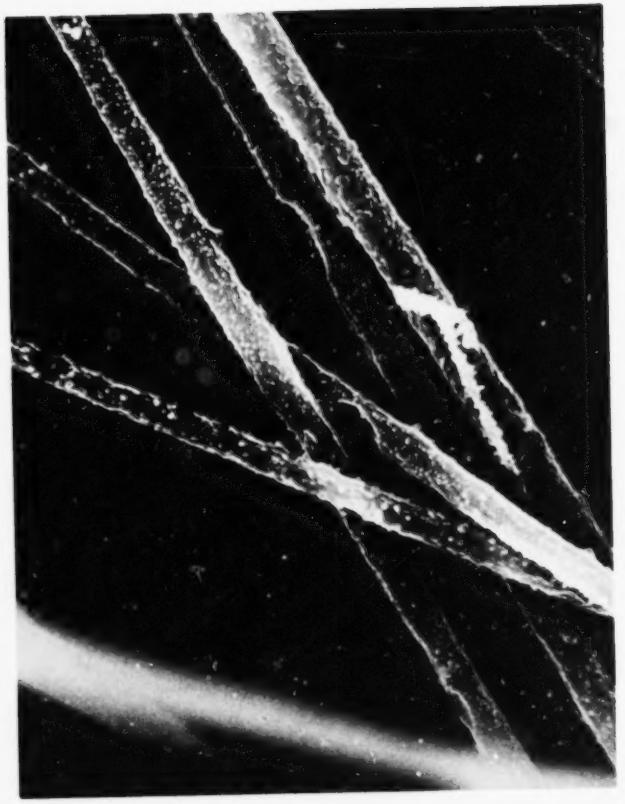


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Figure 9. Carbon fibers from pan composite, heated at 900 C.

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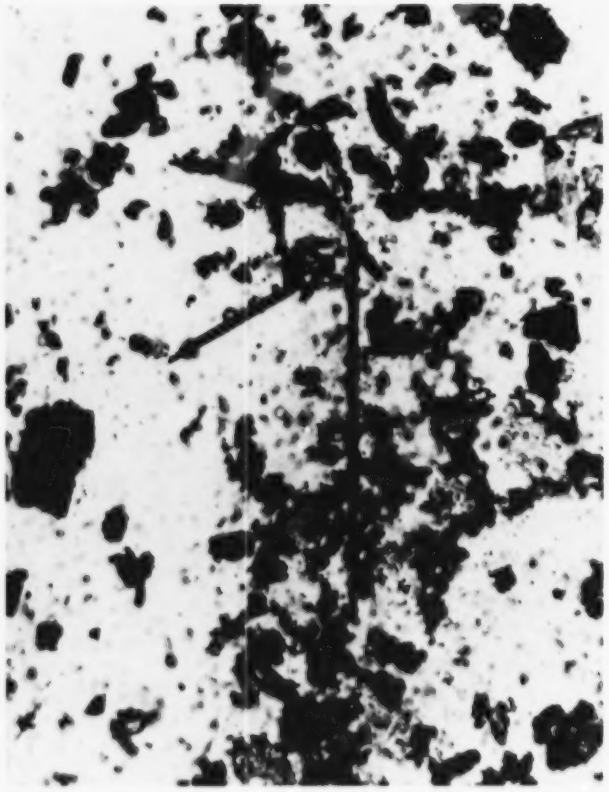

250 X

Figure 10. 10 μ cyclone sample containing carbon fibers.

250 X

Figure 11. 10 μ cyclone sample containing carbon fibers - after HNO_3 acid.

considering time and anticipated concentration using a calibrated restricting valve. Figure 12 is a schematic of the sampling setup.

Light microscopic analyses were performed over a selected radial filter area for each sample depending on the length of fibers observed (i.e., the longer the fiber the more the area analyzed to obtain an accurate representation; typically, one-eighth of the 47-mm filter area was analyzed). All carbon fibers observed in the radial section being analyzed were counted and individual lengths and widths were measured. Subsequently, fiber number concentrations were calculated knowing sample flow rates and sampling times. The corresponding mass concentrations were calculated from number concentration X average fiber volume (determined by length and width measurements) X an assumed density of 1.85 g/cm^3.

Whereas in all samples the fiber widths were relatively constant, the fiber lengths varied greatly from process to process and were widely distributed within a given sample. Figure 13 is a typical length distribution curve for one sample, fitting the data as closely as possible to a log-normal distribution. Figure 14 is cumulative volume percent distribution. Table 3 summarizes the data obtained on four samples taken at a rewinding operation. Table 4 summarizes the data obtained on samples taken at other carbon fiber manufacturing and processing operations.

For the field samples analyzed it was found that no treatment to remove extraneous particulates was required. This will be typically true of most emission samples from noncombustion processes. Only when the NIOSH clearing method does not produce a suitable specimen for light microscopy because of the presence of too much other particulate matter is it necessary to treat the specimen in boiling HNO_3 or use some other appropriate method. The NIOSH clearing method is a standard procedure for asbestos analysis and involves dissolving Millipore filter in 1:1 mixture of diethyl oxalate and dimethyl phthalate.[7] The ease with which carbon fibers may be identified is demonstrated by Figure 15 showing a carbon fiber among the total particulate material collected after the specimen has been cleared using the NIOSH procedure.

Incineration Sampling

Large-scale laboratory tests were conducted to measure emissions from the incineration of carbon fiber composite with refuse. Attempts were made, within the limited scope of the program, to simulate a situation likely to occur in a municipal incinerator.

A stoker-boiler, designed and constructed to study combustion processes, was used for the incineration study. (See Figure 16.) The facility is capable of feeding fuel at rates up to 75 lb per hour and combustion gases are vented through a 14-inch insulated stack that includes sampling ports. A special sampling platform provides for stack sampling 10 pipe diameters downstream in a straight section of the stack. The burning bed can be observed thus providing additional qualitative information on the combustion of the carbon fiber composites. No particulate control mechanisms were used during this study.

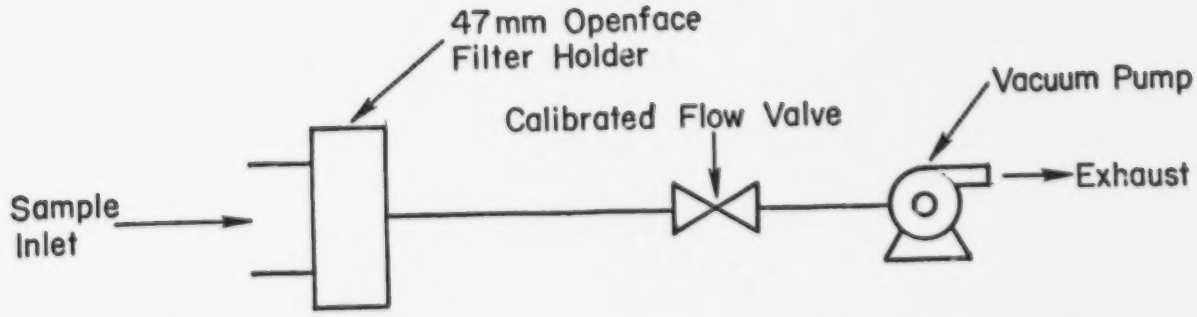

Figure 12. Sampling Setup.

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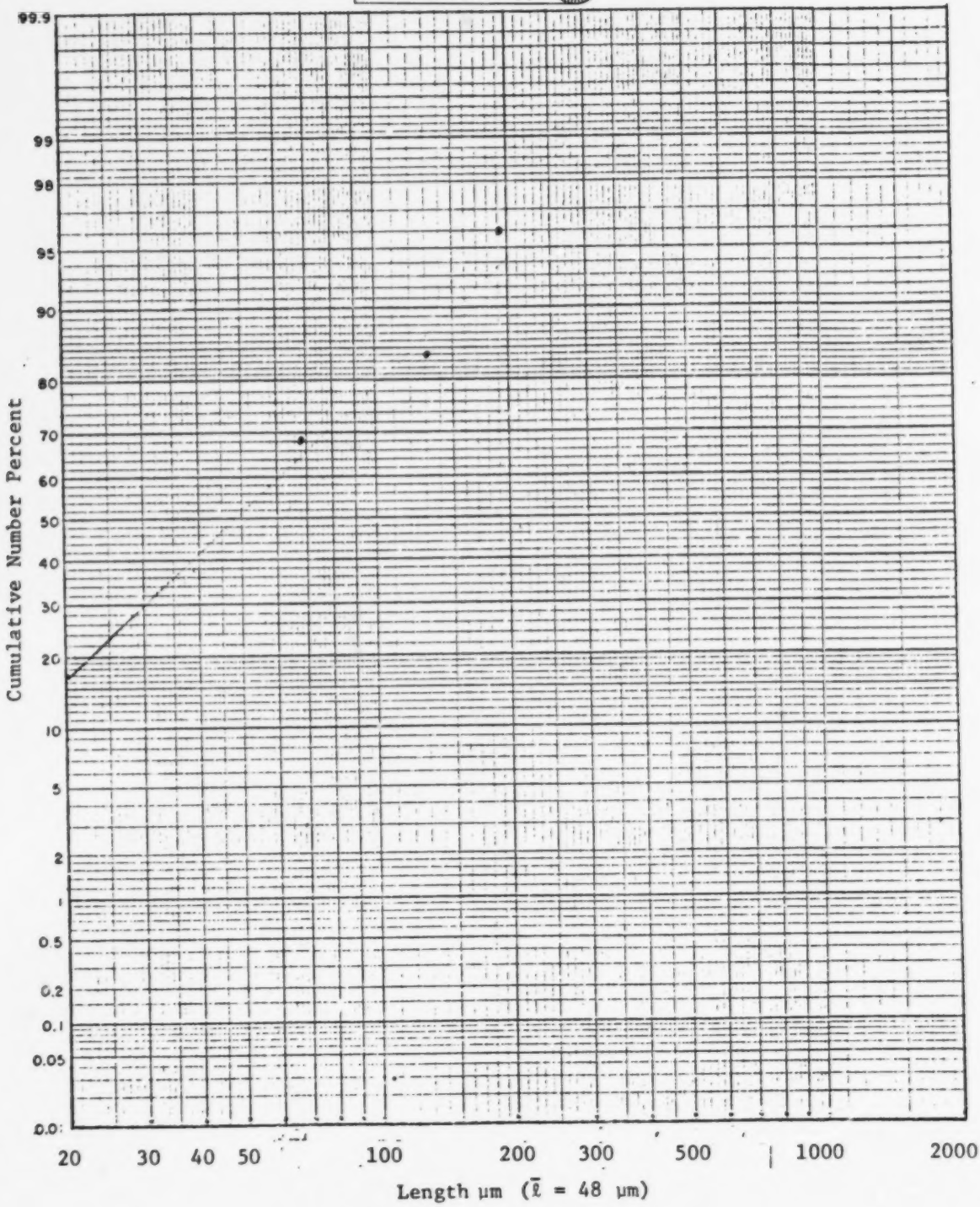


FIGURE 13. SAMPLE 7373-2-01

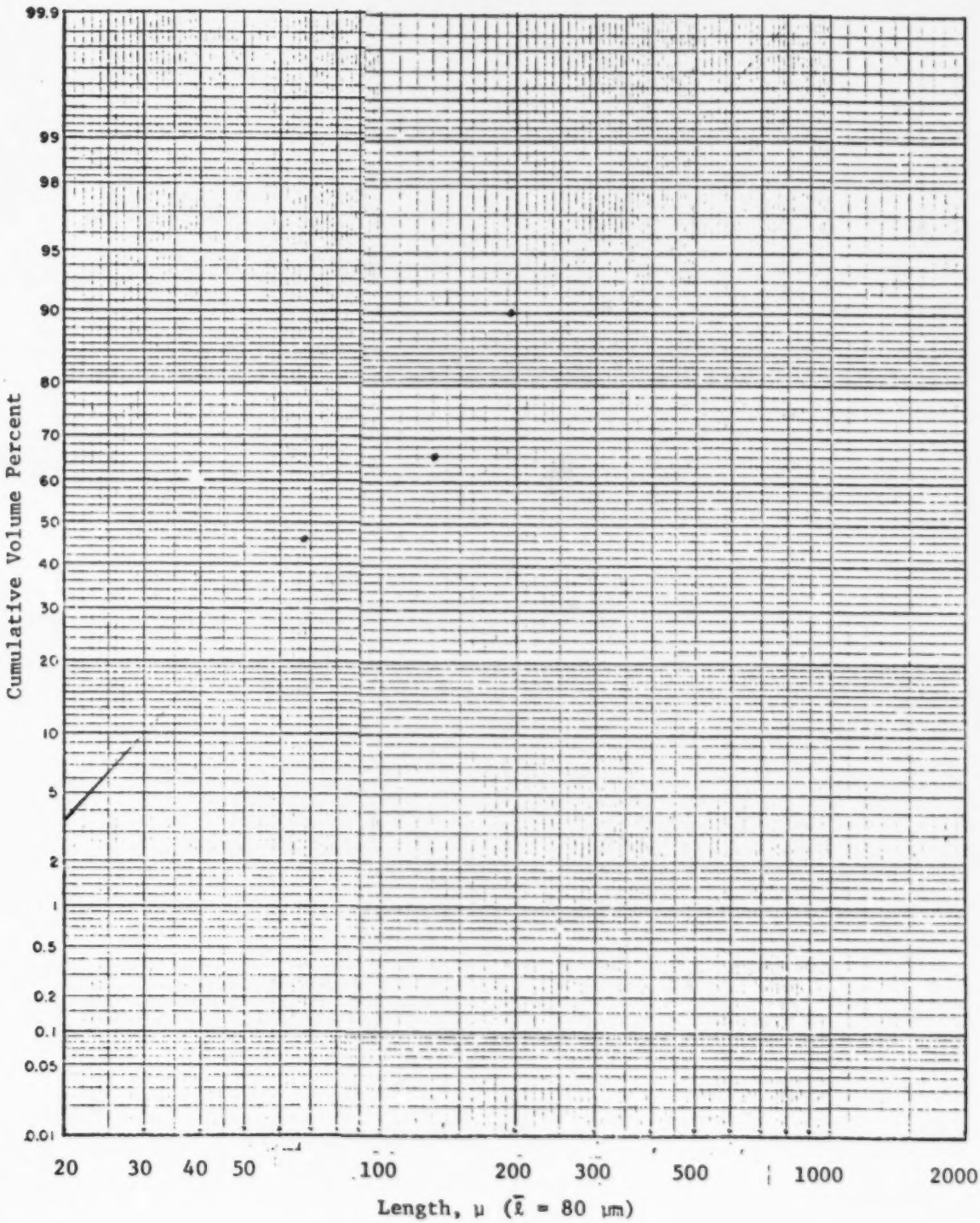


FIGURE 14. SAMPLE 7373-2-01

TABLE 3. RESULTS OF CARBON FIBER ANALYSES OF REWIND SAMPLES

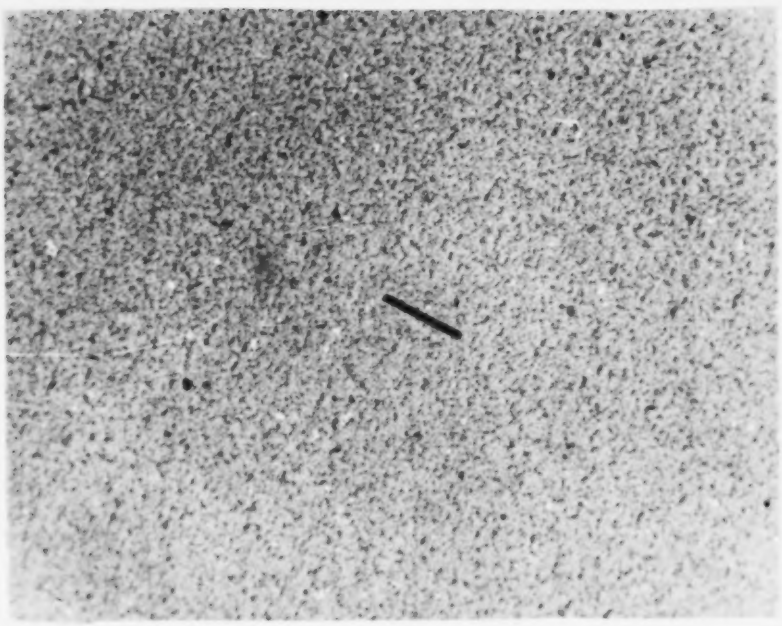
Sample No.	Fibers/m^3	Mass ng/m^3	$\bar{\ell}n$ (μm)(1)	$\bar{\ell}v$ (μm)(2)	d (μm)
7373-2-01	28	211	48	80	6.5
7373-2-02	60	511	60	100	6.5
7373-2-03	32	296	60	110	6.5
7373-2-04	64	908	50	140	6.5

(1) $\bar{\ell}n$ = average length with respect to numbers of fibers.
(2) $\bar{\ell}v$ = average length with respect to fiber volume (or mass).

TABLE 4. CARBON FIBER ANALYSES OF FIELD COLLECTIONS

Operation(a)	Average Length (μm)	Average Width (μm)	Number Concentration (fibers/m^3)	Mass Concentration (ng/m^3)
Prepregging	213.1	6.1	24	356
Shuttle Loom Weaving	749.4	6.7	88	5,497
Machining(b)	30.9	6.6	823	2,062
Machining	32.8	6.2	1,212	2,812
Rapier Weaving(c)	706.0	3.9	340	6,831

(a) Unless otherwise noted all samples are of outside emissions.
(b) Work area sample.
(c) Outside ambient, downstream of baghouse. Some fibers appeared damaged.



100X

Figure 15. Carbon fiber on cleared millipore filter.

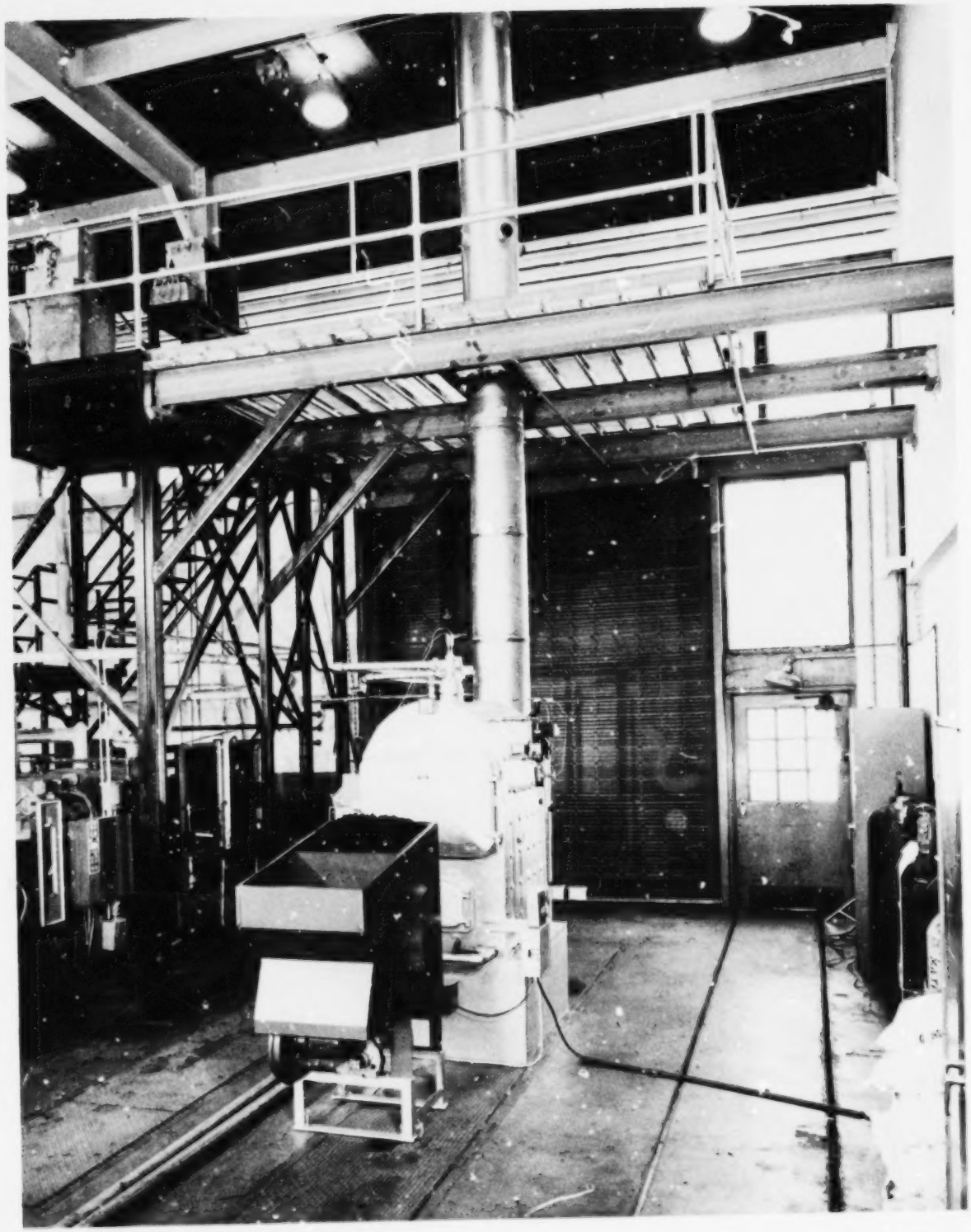


FIGURE 16. STOKER COMBUSTION FACILITY

The carbon fiber composite used for this study was a Celion undirectional type of laminate (nonwoven), with a density of 1.57 g/cc and a fiber content of 62 percent by weight. With no mechanical interlock the fibers should tend to separate upon thermal degradation. The composite was cut into pieces approximately 1 cm x 3 cm x 1/4 cm for feeding into the stoker. The refuse used consisted of a mixture of municipal waste compressed into cylindrical pellets ∿25 mm long x 13 mm diameter.

After reaching a steady state combustion rate of 75 lb/hour of the refuse (flame temperature ∿1700 F, hearth temperature ∿2000 F), 1 lb of the carbon fiber composites was fed onto the burning hearth (along with continual refuse pellet feed) over a 1-minute period.

Sampling was conducted using two modes of collection simultaneously: a Source Assessment Sampling System (SASS) train, using 3 cyclones preceding a filter for the collections (Figure 17), and a Method 17 (in-stack) filter sampling system (Figure 18). The Method 17 filter was changed every 15 minutes in order to provide information on the rate of carbon fiber emissions with time. Care was taken to maintain isokinetic sampling conditions throughout the sampling period.

The samples consisted of three types: (1) bulk particulate brushed from the cyclone catches; (2) cyclone and probe washings deposited on Millipore filters; and (3) Method 17 samples and the SASS train collections on quartz (2500 QAST) filters. For analyses of the incineration samples, the basic sample preparation consisted of sonicating the weighed bulk sample and/or filter in a measured volume (≈10 ml) of filtered deionized water for 15 minutes. Then 25 ml of hot (≈85 C) concentrated nitric acid was added. This was done to destroy extraneous organic materials in the sample that would conceivably interfere with the microscope analysis. After cooling to room temperature, the nitric acid mixture was then diluted to 1000 ml and redeposited in aliquots of 100, 200, and 700 ml on 5.0-μm pore size 47-mm diameter SM Millipore filters. When thoroughly dry, the deposit-bearing filter was transferred to a 2 x 3-inch glass slide. The sample was then cleared using the standard NIOSH solution (1:1 dimethyl phthalate and diethyl oxalate with 0.5 g/ml Millipore filter added) and covered with either glass cover slips or slides.

Analysis was performed by screening samples and original quartz filters at 250 to 400X magnification on a Leitz Orthoplan microscope with transmission objectives. Length and width measurements of either 100+ fibers or 20+ field diameters were made on most samples. Some deposits contained fibers too long to be measured efficiently at higher magnifications. These were scanned at 6.3X in a Wild Photomicroscope. Pictures of the entire cleared deposit were taken using Kodak Plus X-pan black and white film. The prints were then made into a photographic montage and length measurements made of approximately 200 fibers using a photographed millimeter rule for scale. Diameters of these same samples were measured at 250-400X from the cleared deposit using the light microscope. Statistical means of the diameters and lengths were then calculated from the photographic measurements.

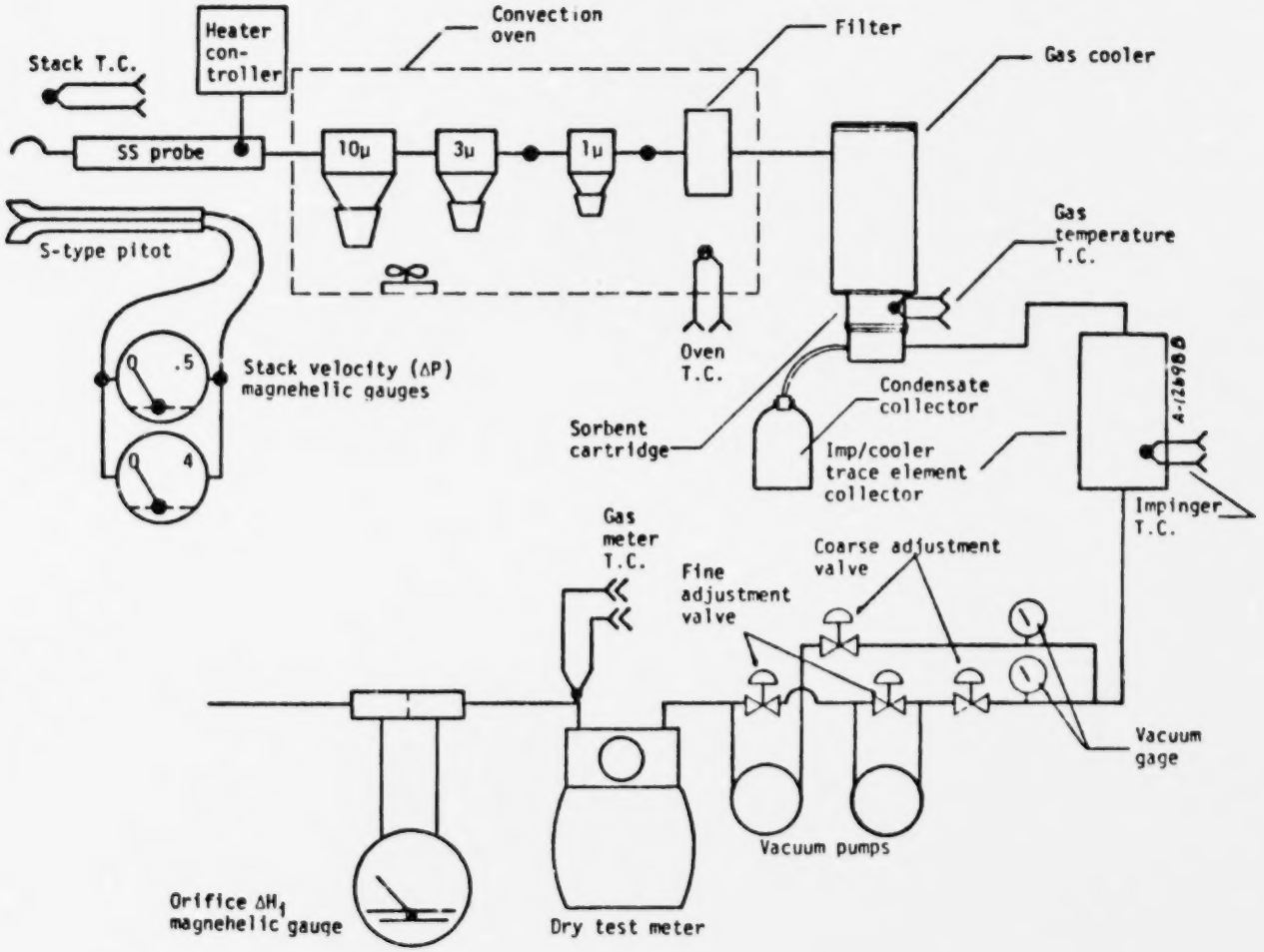
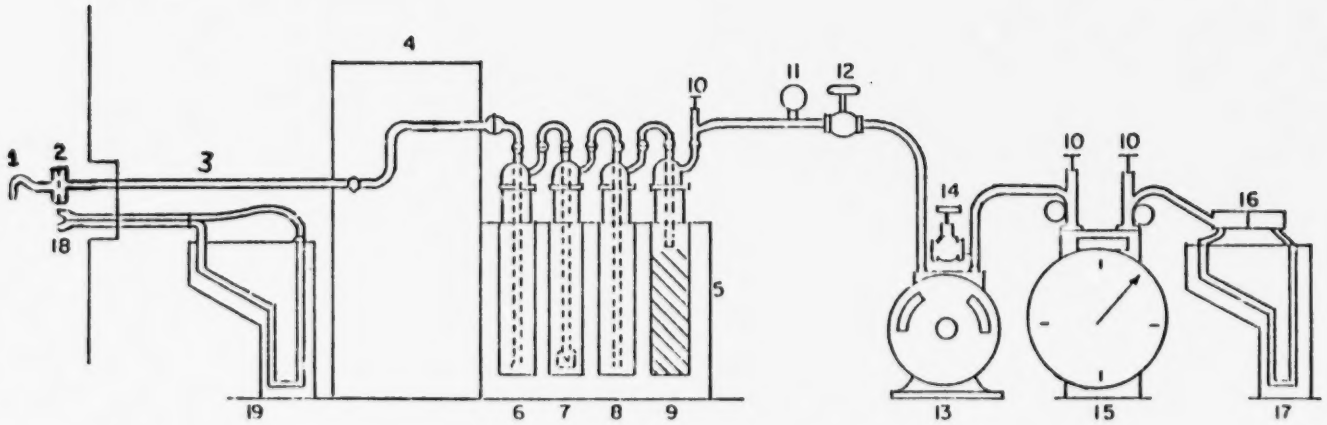


Figure 17. SASS flow diagram.



1. Stainless steel nozzle
2. 47 mm filter
3. Heated probe
4. Method 5 filter box
5. Ice bath for impingers
6. Modified G-S impinger with 100 ml water
7. Greenburg-Smith impinger with 100 ml water
8. Modified G-S impinger
9. Silica gel trap
10. Thermometers or Thermocouples
11. Vacuum gauge
12. Flow control valve
13. Pump
14. Flow control valve
15. Dry test meter
16. Calibrated orifice
17. Manometer (ΔH)
18. "S" type pilot tube
19. Manometer (ΔP)

Figure 18. Method 17 sampling train.

Observations of the collected fibers revealed that fibers are oxidized during incineration and the widths are reduced resulting in width variations. When they are not oxidized, as in the aforementioned field samples, fiber widths are quite uniform. Oxidation of carbon fibers during incineration occurs nonuniformly producing dimples or notches in the fibers. It has been observed in the laboratory that as oxidation proceeds further the fiber is cut in two at the site of the notch resulting in relatively short lengths of carbon fibers with pointed ends. Thus, most oxidized fibers which have small diameters are also expected to be relatively short.

Table 5 shows the results of the incineration study in terms of emission rates. The total emission rates as measured by the SASS train (61.0 mg/dscm particulate; 0.998 mg/dscm carbon fiber) agree reasonably well with those measured by Method 17 (73.0 mg/dscm particulate; 0.840 mg/dscm carbon fiber) given the nature of the experiment, i.e., the Method 17 sampling had to be halted momentarily each 15-minute period for a filter change. Inspection of the Method 17 emission rate data also reveals a decay in fiber emission rate with time as one would expect considering the single point (with respect to time) introduction of the fiber composite into the stoker. This phenomenon is shown graphically in Figure 19. The carbon fiber emission rates display a nearly exponential decay in time whereas the total particulate emission rate is constant within normal operating bounds.

Table 6 is a breakdown of the results by the individual samples. It is interesting to note that nearly all of the carbon fibers (99.6 percent) are captured in the first two cyclones whereas only a relatively small portion (17.1 percent) of the total particulate matter was collected by these cyclones. For these carbon fiber emissions this is not surprising given that their aerodynamic diameter (approximately one and one-half the physical diameter given in Table 3 is on the order of 10 μm). This observation provides promise that cyclones may be used to separate the carbon fibers from extraneous particulate material thus facilitating ease of analysis.

TABLE 5. INCINERATION TEST EMISSIONS RATE

Sample	Sample Volume (dscm)	Total Particulate (mg/dscm)	Carbon Fiber (mg/dscm)	Carbon Fiber (Fibers/dscm)
SASS Train	7.88	61.0	0.998	4310
Method 17				
Pretest	0.295	57.6	0.003	--
0-15 min	0.293	63.8	1.40	--
15-30 min	0.291	70.1	0.62	--
30-45 min	0.287	52.6	0.45	--
45-60 min	0.286	47.6	0.24	--
Nozzle Rinse	1.452	14.6	0.30	
TOTAL Method 17	1.452	73.0	0.84	

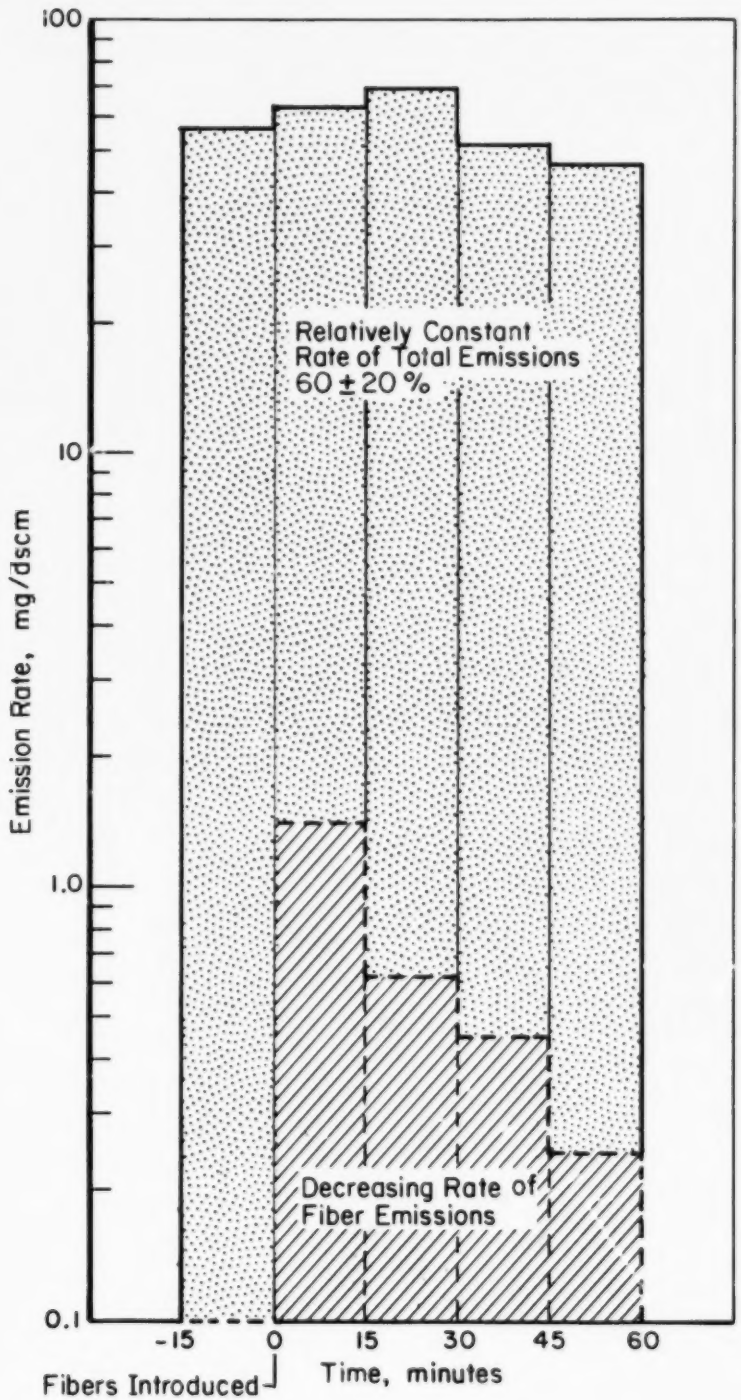


Figure 19. Rates of carbon fiber and total particulate emissions.

TABLE 6. RESULTS OF INCINERATION STACK SAMPLING

Sample	Total Particulate (mg)	Carbon Fiber (mg)	% Carbon Fiber	% of Total Carbon Fiber Sample	Average Length (μm)	Average Width (μm)
SASS Train						
10 μm Cyclone	58.3	6.33	10.9	80.5	5534	4.98
3 μm Cyclone	16.7	1.50	9.0	19.1	1320	3.45
1 μm Cyclone	0.4	0	0	0	--	--
Probe	13.3	0.03	0.23	0.4	108	2.94
Filter	391.8	0.0005	0	0	55	5.6
TOTAL SASS	480.5	7.86	1.64			
Method 17						
Pretest	17.0	0.001	<0.01	0.1	--	--
0-15 min	18.7	0.41	2.19	33.6	--	--
15-30 min	20.4	0.18	0.88	14.8	--	--
30-45 min	15.1	0.13	0.86	10.7	--	--
45-60 min	13.6	0.07	0.51	5.7	--	--
Nozzle Rinse	21.2	0.43	2.03	35.2	--	--
TOTAL Method 17	106.0	1.22	1.15			

SECTION 5

ANALYTICAL PROCEDURE FOR CARBON FIBER EMISSIONS

The analytical procedure for carbon fibers has been designed to yield quantitative results which express numbers and mass of carbon fibers per cubic meter of sampled air volume and/or per unit mass of collected particulate sample. Since carbon fiber sizes are large enough to be resolved by light microscopy, only light microscopy was employed to perform counts and fiber measurements over known areas of filtered deposits.

Specimen preparation for light microscopy and the optical conditions employed during analysis have been selected to eliminate interferences from organic extraneous particulate and fibers other than carbon fibers. Carbon fibers, being opaque, produce high image contrast and therefore do not require phase contrast optics to detect. Consequently, glass fibers, cellulosic fibers, and transparent mineral fibers can be rendered almost invisible by mounting the filter-bearing dispersed particulate in a medium (Type A immersion oil - 1.5150) which has a refractive index near that of the transparent fibers and using a relatively large condenser aperture to observe the fibers in transmitted light. Then, only the opaque carbon fibers are visible. Interference by extraneous organic particulate is reduced in Battelle's procedure by nitric acid treatment.

Fiber lengths have been found to vary widely requiring a range of magnifications to perform measurements. Widths of carbon fiber emissions are quite uniform except those which have been oxidized as from incinerator sources. Most oxidized fibers will have diminished diameters and relatively short lengths. These fibers require higher light microscope magnification (~400X) to be used for fiber counting and measurement.

Relatively long lengths, as great as 10 centimeters, are encountered commonly but not with greatly reduced widths. Consequently low magnifications (~10X) can be employed for length measurements. Precise width measurements of those longer fibers require higher magnifications (from 100 - 400X).

Membrane Filter and Direct Particulate Collection

It is anticipated that most collections of particulate emissions from manufacturing and processing emission streams will be made on mixed ester membrane filters such as Millipore. In this case, the following steps constitute the analytical procedure.

1. Air integrated collections, contained on 47-mm diameter filters; brushings or washes from cyclone collection and other particulate collections with no filter involved are handled similarly to membrane filter collections.

2. The entire filter is immersed in 10 ml of filtered deionized water contained in a 150-ml beaker and sonicated for 15 minutes to loosen the fibers from each other and the filter substate.

3. Then, 25 ml of concentrated nitric acid is added to the sonicated sample and the mixture is heated to below boiling temperature (82 C/180 F) to destroy the filter material and extraneous organic particulate matter.

4. The nitric acid solution containing the fibers is cooled to room temperature and washed and rinsed into a one liter beaker using filtered deionized water.

5. After dilution to one liter, the solution containing the fibers is rapidly whirled to obtain a uniform suspension and aliquots of 100, 200, and 700 ml are vacuum deposited onto three 47-mm diameter, 5.0-um pore size Millipore filters.

6. The fibers containing the redeposited fibers are dried in a laminar flow clean hood.

7. The dried filters are placed onto 2-inch by 3-inch glass microscope slides, cleaned with the NIOSH cleaning solution (1:1 dimethyl phthalate and diethyl oxalate containing 0.5 g/ml of dissolved Millipore material), and covered with glass coverslips and systematically scanned with the light microscope to count and measure carbon fibers over known sample areas, or alternatively, take low magnification micrographs of the preparation, make photographic enlargements, and measure the fiber dimensions from the photographs.

8. Counts and measurements of carbon fibers observed over measured filter areas are made and calculations of carbon fiber concentrations and size distributions are made from these data. Fiber length and width measurements are used in the calculation of fiber volume by multiplying length times width squared; volume in turn is coverted to mass by multiplying by the density 1.85 g/cc. Calculational procedures must be conducted as dictated by sampling times, air flow rate, filter areas, dilutions, aliquot sizes, and magnifications.

Glass or Quartz Filter Collections

Particulate samples on glass or quartz filters require an additional treatment since particulate matter is present also embedded in the filter structures of these. Glass or quartz filter collections are treated similarly to those on membrane filter as described above but additionally (in step 4 above) the undissolved filter is thoroughly washed and withdrawn from the 1-liter dilution solution. After drying, the particulate trapped beneath the fiber filter surface is examined by mounting the filter in matching microscope immersion oil to make the glass or quartz fibers invisible. Carbon fibers are counted and measured by light microscopy in the resulting preparation and the data combined with the data obtained on fibers removed by sonication. Note: When glass or fiber filter collections are preceded by cyclone catches as in a SASS train assembly, only a very few fibers are contained on the filters.

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